(12) UK Patent Application (19) GB (11) 2 310 862 (13) A

(43) Date of A Publication 10.09.1997

(21) Application No 9704546.2

(22) Date of Filing 05.03.1997

(30) Priority Data
(31) 9604670 (32) 05.03.1996 (33) GB

(71) Applicant(s)
Huw Trefor Morris
1 Laburnum Close, Creswell, NR WORKSOP, Nottinghamshire, S81 4AD, United Kingdom

(72) Inventor(s)
Huw Trefor Morris

(74) Agent and/or Address for Service
Appleyard Lees
15 Clare Road, HALIFAX, West Yorkshire, HX1 2HY, United Kingdom

(51) INT CL[6]
C03C 17/28 , C09D 167/06

(52) UK CL (Edition O)
C3V VBC
B2E EM E1740 E415S E444T E481T E489T
C1M MWC M408
C3W W225 W228
U1S S1386 S1397 S1855 S3042 S3043

(56) Documents Cited
GB 1526926 A EP 0615980 A2 EP 0548740 A1
EP 0108630 A2 WO 92/21579 A1 US 4840551 A
US 4197333 A US 3840390 A

(58) Field of Search
UK CL (Edition O) C1M MWC , C3V VBC
INT CL[6] C03C
Online: WPI

(54) Resin formulations

(57) A resin formulation is disclosed for treating or coating glass, especially for repairing imperfections, for example cracks in automobile windscreens, the formulation being curable by daylight or UV light. The composition may have a viscosity of more than 5 centipoises and may comprise polyester acrylate, methyl methacrylate, benzoyl peroxide and vinyl methoxysilane.

GB 2 310 862 A

RESIN FORMULATIONS

The present invention relates to resin formulations especially for repairing imperfections in glass members.

A common problem with glass sheets, for example automobile windscreens, or laminated glass sheets for shop fronts, is the propagation of cracks and damage through impacting articles on to the glass. For example, shop fronts may suffer elongate cracks which propagate over part of a large pane of glass, for example in a corner, but which necessitate replacement of the whole glass sheet.

Similarly, automobile windscreens may suffer star bursts, bulls eye chips, and cracks.

It is known to repair cracks and other damage to glass sheets using a clear fluid resin which may be forced into a crack, and which may then set, bonding the crack together. Devices for injecting and applying such resins are disclosed in US 4,775,305, US 4,753,695 and US 3,562,366, which are examples of apparatus for repairing glass sheets.

The conventional apparatus for repairing glass sheets requires a resin which is initially in fluid form and hardens upon exposure to ultra violet light when injected into a crack.

In the applicants co-pending UK patent application 96 26983.2, the full contents of which are incorporated herein by reference, there is disclosed an improved glass sheet repair device which operates by injecting a fluid resin

into a crack. Once in the crack, the fluid mixes with air trapped in the cracked or damaged area. The fluid is then withdrawn out of the damaged area by the device, drawing with it trapped air. The trapped air is then separated from the fluid in the repair device, prior to re-injecting the fluid into the damaged glass area. Repeated injection and withdrawal of the fluid may be required in order to purge all trapped air from the resin and the damaged glass area.

Conventional glass repair resins are unsuitable for the operation of the improved glass repair device. The known resins have a problem of being unable to be withdrawn from the crack once injected into the crack, of poor separability of entrapped air from the resin, of incorrect viscosity for repeated injection and withdrawal to a damaged glass area, poor flowability, leading to inadequate flow into the damaged glass area through capillary action or pressurised injection, and unsatisfactory curing from fluid to solid state.

According to the invention, there is provided a method of treating a transparent member, especially a glass member, the method comprising contacting the member with a resin formulation, wherein the resin formulation has a viscosity of greater than 5 centipoise and is curable under exposure to normal daylight.

By normal daylight, we mean that the ambient light need not comprise intense sun. The resin formulation may be curable in overcast conditions. Alternatively, the resin formulation may be curable using an ultraviolet light source. In this case, the resin formulation may be curable in less than 5 minutes, preferably less than 3 minutes, more preferably less than 1 minute, especially less than 30 seconds.

Said method is preferably a method of repairing an imperfection of a transparent member.

Said imperfection may be a crack or cavity or may be a surface defect. It is preferably a crack or cavity which extends below the surface of the transparent member.

Said resin formulation is preferably substantially colourless when cured and preferably also when uncured. Said resin formulation preferably has a refractive index which is substantially equal to the refractive index of the transparent member with which it is contacted so that the imperfection and/or the resin formulation are substantially invisible after repair of the imperfection. Said resin formulation is preferably substantially transparent when cured

Said viscosity may be greater than 10 centipoise, preferably greater than 20 centipoise, more preferably greater than 30 centipoise, especially greater than 50 centipoise. Said resin formulation preferably has a syrup like viscosity.

Said resin formulation suitably comprises a polymerisable material which preferably includes alkenyl functional groups. Said formulation preferably includes a material having an ester functionality. Said formulation preferably includes an acrylate based material, with an alkyl, especially methyl, methacrylate being especially preferred. Said formulation may also include a polyester acrylic material.

Preferably, over 80 wt%, more preferably over 90 wt%, especially over 95 wt% of said formulation comprises polymerisable material. Said polymerisable material may include at least 10 wt%, preferably at least 20 wt%, especially at least 25 wt% of an acrylate material. Said formulation may include two types of polymerisable material.

Said resin formulation preferably includes a free radical initiator which is suitably a peroxide, especially an aromatic peroxide, with benzoyl peroxide being especially preferred. Said formulation may include less than 1 wt%, preferably less than 0.5 wt%, more preferably less than 0.1 wt%, especially less than 0.05 wt% of said initiator.

Said formulation preferably includes a photopolymerisation catalyst suitably at a weight of less than 1 wt%, preferably less than 0.5 wt%, more preferably less than 0.1 wt%, especially less than 0.05 wt%. Benzoin is a preferred catalyst.

Said formulation preferably includes an intermediary compound for increasing the ability of the formulation to bond to an inorganic material for example glass. Said intermediary compound may be a silane, preferably an organo-functional silane, more preferably a silane substituted alkene moiety, especially a vinyl silane compound, for example vinyl alkoxy, especially methoxysilane. Said intermediary compound may be present at a weight of less than 1 wt%, preferably less than 0.5 wt%, especially less than 0.01 wt%.

The invention extends to the use of a resin formulation as described for treating a transparent member, especially for repairing an imperfection of a transparent member.

The invention extends to a resin formulation per se for repairing an imperfection of a transparent member.

According to one aspect of the present of the present invention there is provided a substantially transparent resin formulation capable of curing from a fluid state to a solid state under exposure to light, the resin formulation having fluid viscosity selected such as to allow repeated injection or withdrawal of the fluid into or out of a damaged area of a glass sheet, under exposure to normal daylight.

Preferably the resin formulation is capable of setting from a fluid state to a solid state, under conditions of normal daylight levels, within a period of twenty minutes.

The damage may include cracks, starbursts, bullseyes or chips. Particularly but not exclusively, the viscosity is selected so as to allow repeated injection and withdrawal into or out of cracks in a glass sheet.

Preferably the resin formulation is capable of flowing into or out of damage in a glass sheet, under normal daylight conditions, for a period of one to five minutes, prior to entering a substantially non-flowable state in which the resin formulation cannot be injected into or withdrawn from the glass.

The resin formulation may comprise a resin formulation according to the second aspect hereunder.

According to a second aspect of the present invention there is provided a resin formulation comprising:

a base constituent; and

an ultra violet active constituent capable of setting the base constituent from a fluid state to a solid state upon exposure of the resin formulation to normal daylight.

Preferably, the base constituent comprises a polymeric material.

The resin formulation may comprise a peroxide eg. benzoyl peroxide, and/or benzoin.

The resin formulation may comprise an acrylic eg. polyester acrylic, and/or methyl methacrylate.

The resin formulation may comprise vinyl methoxysilane.

Preferably the ratio of benzoyl peroxide and/or benzoin to polyester acrylic and/or methyl methacrylate and are in the following ratios:

Benzoyl peroxide and/or benzoin 6 to 10 parts by weight.

Polyester acrylic and/or methyl methacrylate 0.1 to 0.7 parts by weight.

Suitably, a ratio of benzoyl peroxide and/or benzoin to polyester acrylic and/or methyl methacrylate in the following ratios has been found to give good results:

Benzoyl peroxide and/or benzoin 7.27 ± 10% parts by weight.

Polyester acrylic and/or methyl methacrylate 0.255 ± 10% parts by weight.

Suitably the acrylic/methyl methacrylate is present in the following ratios:

Polyester acrylic 7 ± 20% parts by weight.

Methyl methacrylate 3 ± 20% parts by weight.

Advantageously, the polyester acrylic/methyl methacrylate is present in the following ratios:

Polyester acrylic 7 ± 10% parts by weight.

Methyl methacrylate 0.27 ± 10% parts by weight.

Suitably, the benzoyl peroxide/benzoin/methyl methacrylate is present in the following ratios:

Benzoyl peroxide 0.03 ± 20% parts by weight.

Benzoin 0.1 ± 20% parts by weight.

Vinyl methoxysilane 0.025 ± 20% parts by weight.

Advantageously, the benzoyl/peroxide/benzoin/methyl methacrylate is present in the following ratios:

Benzoyl peroxide 0.03 ± 10% parts by weight.

Benzoin 0.2 ± 10% parts by weight.

Vinyl methoxysilane 0.025 ± 10% parts by weight.

The invention includes a method of repairing a damaged glass sheet, the method comprising the steps of:

injecting a fluid resin formulation into a crack or damaged area of the glass sheet;

withdrawing the resin formulation from the crack or damaged area;

separating out air from the resin formulation;

re-injecting the resin formulation into the crack or damaged area of the glass.

The method may include repetitions of the above steps.

The resin formulation may comprise a resin formulation according to the second aspect described herein above.

According to a third aspect of the present invention, there is provided a sheet of glass material having a surface coating of a clear polymeric resin formulation.

The glass sheet may have two sides and be coated on both sides with said resin formulation.

The resin formulation is preferably a resin formulation capable of changing from a fluid state to a solid state under normal daylight conditions.

The invention includes a sheet of glass coated on one or a plurality of sides with a resin formulation according to the above aspects.

The resin formulation may comprise a resin according to the second aspect herein above.

For a better understanding of the invention, and to show how the same may be carried into effect, there will now be described specific embodiments and methods according to the present invention.

To repair a crack, star burst, bullseye, chip or other damage in a glass sheet, eg. using a device such as described in co-pending UK patent application number 96 26983.2, a suitable specific embodiment resin formulation has been experimentally developed as follows:

The resin formulation comprises a base constituent, and an ultra violet active constituent which causes the base constituent to undergo a transition from a liquid state to a solid state under daylight conditions.

The resin formulation is capable of being injected and withdrawn from a damaged glass region whilst in a fluid state. The resin formulation is of flowability and viscosity such as to be workable over a period of one to five minutes without hardening to a substantially non-flowable state.

Suitably, the base constituent comprises a mixture of polyester acrylic and methyl methacrylate.

A ratio of polyester acrylic to methyl methacrylate which has been found to give the optimum performance for injection and withdrawal into the damaged glass, in normal daylight, whilst allowing purging of air from the resin formulation, is as follows:

Polyester acrylic ± 20% parts by weight.

Methyl methacrylate 0.27 ± 20% parts by weight.

It is thought that the light sensitive constituent comprises benzoyl peroxide, and/or benzoin, and/or vinyl methoxysilane.

The resin formulation comprises benzoyl peroxide, benzoin and vinyl methoxysilane in the following relative proportions.

Benzoyl peroxide 0.03 ± 20% parts by weight.

Benzoin 0.2 ± 20% parts by weight.

Vinyl methoxysilane 0.025 ± 20% parts by weight.

When the resin liquid formulation is injected into the damaged area of glass, there may be trapped air bubbles within the glass damaged area. To remove air bubbles, captured by the resin formulation, the resin formulation is drawn out of the glass. The trapped air has been found to separate from the resin formulation under gravity, when the resin formulation is removed from the damaged glass area.

The operation may be repeated until all air bubbles in the liquid are removed.

The resin formulation is found to have adequate properties of flowability into the damaged glass sheet, either for injection into or withdrawal from the damaged area, have good separation qualities of air from resin formulation, and reasonable curing time in the range 5 to 20 minutes.

The resin formulation sets under ultra violet light of intensity as found in normal daylight conditions, and has a refractive index equivalent of that of glass, thus effecting a virtually invisible repair.

By use of the resin formulation in a vacuum creating chamber, separation of air from the resin formulation is possible, against gravity, and the resin formulation may be suitable for use in a glass repair device used in an inverted position to repair glass damage from underneath.

Any feature of any aspect of any invention, example or embodiment described herein may be combined with any feature of any aspect of any other invention, example or embodiment described herein.

Two specific embodiments of the resin formulation were tested practically. The relative compositions of the specific embodiments in parts by weight were as follows:

Resin formulation A

Polyester acrylic	7 parts
Methyl methacrylate	3 parts
Benzoyl peroxide	0.03 parts
Benzoin	0.1 parts
Vinyl methoxysilane	0.025 parts

Resin formulation B

Polyester acrylic	7 parts
Methyl methacrylate	0.27 parts
Benzoyl peroxide	0.03 parts
Benzoin	0.2 parts
Vinyl methoxysilane	0.025 parts

It was found experimentally, that whilst resin formulation A was difficult to work into and out of a damaged glass area, being of higher viscosity and quicker hardening or curing time in daylight, the resin formulation B proved to have good workability and flowed into and out of cracks, had lower viscosity and increased hardening time in normal UK daylight conditions.

According to a specific embodiment of the present invention, a glass sheet eg. an automobile windscreen or toughen glass planar sheet may be coated on one or both sides with the resin formulation as described above. Coating of the glass sheet may improve the crack and damage resistant properties of the glass. For example, as a replacement for a conventional laminated glass sheet having inner and outer glass layers sandwiching a central polymer layer, there may be provided according to a specific embodiment of the present invention a glass sheet having a central glass layer, sandwiched between first and second outer layers of resin. The resin formulation may be applied to first and second sides of the glass by spraying, applying the resin formulation with a brush or otherwise coating the glass layer. The glass may then be exposed to daylight or ultra violet light, in order to cure the resin formulation to set to a solid state.

It is has been found experimentally that a glass sheet coated with the resin formulation shows no discolouration when subjected to temperatures below freezing, and is weather resistant.

A glass sheet coated as above may have blast-proof or impact resistant properties.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A method of treating a transparent member, especially a glass member, the method comprising contacting the member with a resin formulation, wherein the resin formulation has a viscosity of greater than 5 centipoise and is curable under exposure to normal daylight.

2. A method according to claim 1 which is a method of repairing an imperfection in said transparent member.

3. A method according to claim 1 or claim 2, wherein said resin formulation is substantially colourless when cured.

4. A method according to any preceding claim, wherein said resin formulation has a refractive index which is substantially equal to the refracted index of the transparent member with which it is contacted.

5. A method according to any preceding claim, wherein said resin formulation has a viscosity of greater than 10 centipoise.

6. A method according to any preceding claim, wherein said resin formulation has a viscosity of greater than 50 centipoise.

7. A method according to any preceding claim, wherein said resin formulation comprises a polymerisable material.

8. A method according to any preceding claim, wherein said resin formulation includes a polymerisable material which includes alkenyl functional groups.

9. A method according to any preceding claim, wherein said resin formulation includes a polymerisable material which includes ester functional groups.

10. A method according to any preceding claim, wherein said resin formulation includes an acrylate based material.

11. A method according to any preceding claim, wherein over 80 wt% of said resin formulation comprises polymerisable material.

12. A method according to any preceding claim, wherein said resin formulation includes a free radical initiator.

13. A method according to claim 12 wherein said free radical initiator is a peroxide.

14. A method according to claim 12 or claim 13, wherein said resin formulation includes less than 1 wt% of said free radical initiator.

15. A method according to any preceding claim, wherein said resin formulation includes a photopolymerisation catalyst.

16. A method according to claim 15, wherein said photopolymerisation catalyst is present at a weight of less than 1 wt%.

17. A method according to claim 15 or claim 16, wherein said photopolymerisation catalyst is benzoin.

18. A method according to any preceding claim, wherein said resin formulation includes an intermediary compound for increasing the ability of the formulation to bond to an inorganic material.

19. A method according to claim 18, wherein said intermediary compound is a silane.

20. A method according to claim 18 or claim 19, wherein said silane is an organo-functional silane.

21. A method according to claim 19 or 20, wherein said intermediary compound is present at a weight of less than 1 wt%.

22. Use of a resin formulation as described in any of claims 1 to 21 for treating a transparent member.

23. A resin formulation per se as described in any of claims 1 to 21 for repairing a transparent, especially for repairing an imperfection of a transparent, member.

24. A method substantially as hereinbefore described with reference to the examples.

25. A use substantially as hereinbefore described with reference to the examples.

26. A resin substantially as hereinbefore described with reference to the examples.

Application No: GB 9704546.2
Claims searched: 1-26

Examiner: K. Macdonald
Date of search: 20 May 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3V(VBC); C1M(MWC)

Int Cl (Ed.6): C03C

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB1526926	(MMM) see Claim 1; page 4, lines 5-54; page 6, line 42	23 at least
X	EP 0615980 A2	(CIBA-GEIGY) see Claim 18	23 at least
X	EP 0548740 A1	(ROHM) see Claim 1	23 at least
X	EP 0108630 A2	(DELTAGLASS) see Examples	23 at least
X	WO 92/21579 A1	(ADVANCED GLASS) see Claim1	23 at least
X	US 4840551	(DAIMLER-BENZ) see column, line 40-column 4, line 2	23 at least
X	US 4197333	(GTE) see column 3, lines 17-19; column 5, lines 49-68	23 at least
X	US 3840390	(KANSAI) see column 1, lines 7-32	23 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family
A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.